

PATENT SPECIFICATION

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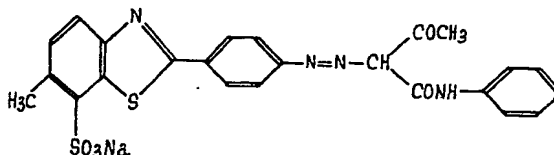
(54) NEW DISAZO DYESTUFFS

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a corporation of Japan, of 15 Kitahama 5-chome, Higashi-ku, Osaka, Japan, do hereby declare this invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

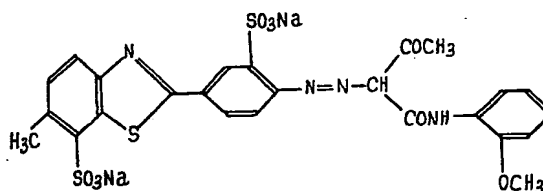
The present invention relates to new yellow dyes for dyeing cellulosic materials, particularly paper and paper pulp.

Among the yellow dyes which have been used for dyeing paper and paper pulp, as bright greenish yellow dyes there are known dyes defined by C.I. Direct Yellow 8 (C.I. No. 13920) and C.I. Direct Yellow 27 (C.I. No. 13950), and as reddish yellow dyes there are known dyes defined by C.I. Direct Yellow 50 (C.I. No. 29025) and C.I. Direct Yellow 12 (C.I. No. 24895), as follows.

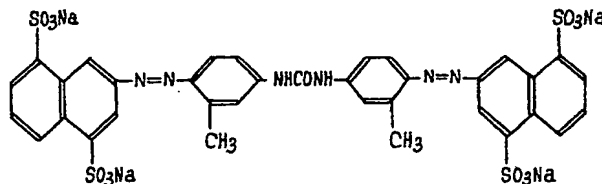
C.I. No. 13920



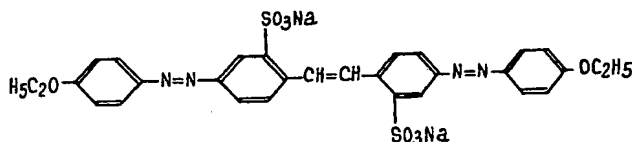
15 C.I. No. 13950



C.I. No. 29025



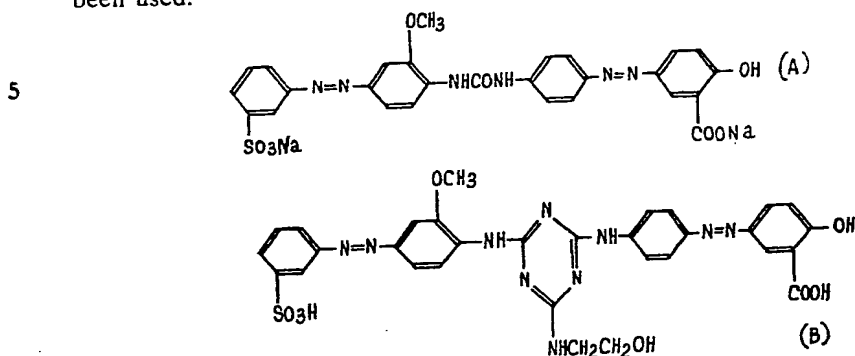
C.I. No. 24895



[Price 33p]

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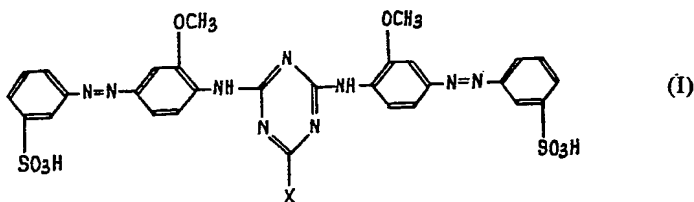
Furthermore, as a neutral yellow dye between the two, a dye defined by C.I. Direct Yellow 44 (C.I. No. 29000) of the formula (A), and a dye of the formula (B) disclosed in Example 3 of Japanese Patent Publication No. 7643/1958 have widely been used.



However, the dye (A) has disadvantageously a low storage stability of aqueous dye solution, and a low affinity to paper pulp thereby causing a problem of staining waste water. The dye (B) has a high affinity to paper pulp, however its solubility is low. In addition, the two dyes (A) and (B) have a disadvantage of changing their shades if the water contains Fe ions.

An object of the present invention is to provide a dye which is free from the effect of change of shade by metal ion, and has a good affinity, solubility and in addition light fastness, by overcoming the disadvantages of the two dyes (A) and (B).

The object can be achieved by providing new dyes which in the form of the free acid have the formula,



wherein X is a mono- or di-(hydroxyalkyl)amino group, and a method for preparing said new dyes characterized by reacting 1 mole of a cyanuric halide with 2 moles of 3-methoxy-4-aminoazobenzene-3'-sulfonic acid and 1 mole of a mono- or di-(hydroxyalkyl)amine in either order.

The inventors have found that when X is, for example, especially a group derived from monoethanolamine, diethanolamine, monopropanolamine or dipropanolamine, most preferably diethanolamine, the dyes have a very high affinity to cellulose, particularly paper and paper pulp, and a high solubility.

The cyanuric halide employed for preparing the dyes of the present invention include cyanuric bromide and preferably cyanuric chloride. 3-Methoxy-4-aminoazobenzene-3'-sulfonic acid is a known intermediate and can be prepared by a conventional method.

The reaction of a cyanuric halide with 3-methoxy-4-aminoazobenzene-3'-sulfonic acid and a mono- or di-(hydroxyalkyl)amine can be carried out in an aqueous medium, if necessary in the presence of an organic solvent, by a stepwise condensation reaction, the first step being at from -10 to 20°C ., the second step being at from 20 to 60°C . and the third step being at from 60 to 110°C . The order of the reaction of the halide with the azobenzene and the mono- or di-(hydroxyalkyl)amine can be altered optionally. In some cases, a surfactant may be added to allow the reaction to proceed smoothly. The desired dyes can be separated as a metal salt thereof by conventional processes such as a salting out, or in a powder form directly by spray-drying of the reaction solution. The dyes can be used for dyeing, in the form of powder, or if necessary, in the form of a liquid formulation. Furthermore, the dyes can be obtained as an ammonium salt or organic amine salt thereof.

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- 5 The dyes of the present invention are particularly suitable for dyeing paper and paper pulp. The dyes can be applied to them by a beater addition process in which the dye solution is added to a pulp liquor under stirring and then the dyed pulp is subjected to the manufacture of paper, or by a size press process in which sheet formed paper is dipped in the dye bath containing a size and press-dried. Furthermore, the dyes can also be used for dyeing cotton and rayon by a conventional exhaustion dyeing process or padding process, and particularly advantageously for dyeing polyester/cotton blended yarns by a one-bath high temperature dyeing process.
- 10 As mentioned above, the dyes of the present invention are suitable for dyeing natural and regenerated cellulosic fibers, paper and paper pulp, to give neutral yellow dyeings with an excellent lightfastness. The dyes have superior properties to the conventional dyes (A) and (B) as shown in the following Table in which the present dye (I) is the dye obtained in Example 1 below.

TABLE

Property	Dye		
	The present dye (I)	Known dye (A)	Known dye (B)
Solubility (g/l.)	80°C.	70	100
	20°C.	25	40
Storage stability of dye liquor	50 g/l.	50 g/l.	30 g/l.
	No change after 3 days	Gel-formation after 3 days	Gel-formation after 3 days
Degree of staining of waste water from pulp-dyeing according to Example 3	Hardly stained	Considerably stained	Hardly stained
Effect of iron ions (1)	Became slightly reddish	Became very reddish and dark	Became very reddish and dark
Light fastness (2) (non-size paper)	5	4	4 - 5

Note:

(1) A pulp-dyeing test with an addition of ferric chloride (FeCl_3) corresponding to 10 p.p.m. of ferric ion.

(2) Rated by the Grey Scale according to JIS L 1044, 8 denoting the highest and 1 denoting the lowest

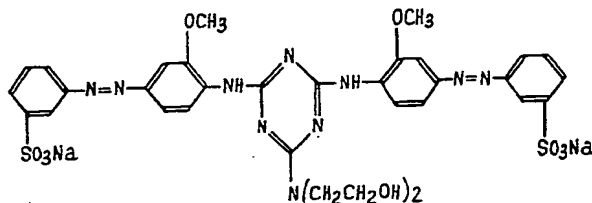
The present invention will be illustrated in more details with reference to the following examples, which are only given for the purpose of illustration and are not to be interpreted as limiting. In the examples, all parts are by weight.

Example 1.

- 20 65.8 parts of sodium 3-methoxy-4-aminoazobenzene-3'-sulfonate were dissolved in 180 parts of water, and 18.5 parts of cyanuric chloride were added thereto at 5°C. Then the solution was heated to from 60 to 65°C. while adjusting the pH of the solution to from 6 to 7 with sodium carbonate, and maintained it at the same temperature for 2 hours while stirring. 30 parts of diethanolamine were added to the solution which was then refluxed to complete the reaction. After salting out the solution with common salt, the precipitates were filtered and dried
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to give 100 parts of a dye in the form of brown powder. The dye thus obtained of the following formula gives dyeings of a yellow shade on cellulosic fibers.



Example 2.

A dye was prepared in the same manner as described in Example 1, except that 30 parts of diethanolamine were replaced by 18 parts of monoethanolamine. 100 parts of a dye in the form of brown powder were obtained. The dye showed the dyeing properties similar to that of the dye in Example 1.

Example 3.

A dye was prepared in the same manner as described in Example 1, except that 30 parts of diethanolamine were replaced by 40 parts of dipropanolamine. 103 parts of a dye in the form of brown powder giving dyeings of a yellow shade on cellulose were obtained.

Example 4.

0.05 part of the dye obtained in Example 1 was dissolved in 250 parts of water to make a dyeing bath. 5 parts of viscose rayon yarns were introduced into the dyeing bath which was then heated to 85°C. After 10 minutes, 0.5 part of Glauber's salt anhydrous was added and dyeing was carried out for 35 minutes. After rinsing, bright yellow dyeings were obtained.

Example 5.

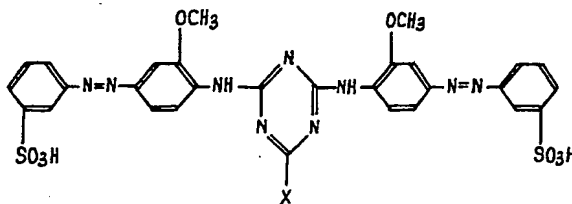
0.05 part of the dye obtained in Example 1, 0.1 part of Sumikaron Yellow SE-5G (a trade name for a disperse dye sold by Sumitomo Chemical Company, Limited), 0.25 part of Sumipon TF (a trade name for a surfactant sold by Sumitomo Chemical Company, Limited) and 0.5 part of Glauber's salt anhydrous were dissolved in 250 parts of water to make a dyeing bath. 5 parts of polyester/rayon blended yarns were introduced into the dyeing bath which was then heated to 90°C. over 20 minutes, and further to 130°C. over 40 minutes. Dyeing was carried out at the same temperature for 60 minutes. After dyeing, the bath was cooled to 90°C. gradually and maintained at the same temperature for 20 minutes. Dyed materials were taken out, rinsed and dried to give dyeings of a bright yellow shade on both the polyester portion and the rayon portion.

Example 6.

0.1 part of the dye obtained in Example 1 was introduced into 500 parts of a pulp liquor containing 20 g. of L.B.K.P. (Laubholz Bleached Kraft Pulp) beaten to 500 C.F. (Canadian Freeeness) per liter of water. After the liquor was thoroughly stirred for 10 minutes, 0.33 part of Size Pine E (a trade name for a size sold by Arakawa Rinsan Co., Ltd.) was added thereto and after 10 minutes 0.3 part of aluminum sulfate crystals was further added. Dyeing was carried out for 20 minutes while stirring. On sheet forming from the pulp liquor, bright yellow colored paper was obtained.

WHAT WE CLAIM IS:—

1. A compound which in the form of a free acid, has the formula,

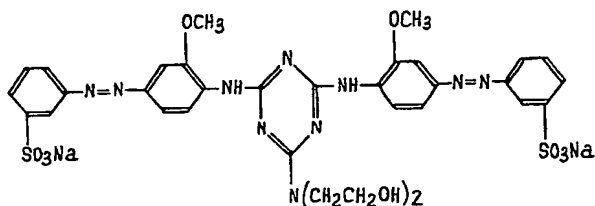


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wherein X is a mono- or di-(hydroxyalkyl)amino group.

2. The compound according to Claim 1, wherein X is a group derived from monoethanolamine, diethanolamine, monopropylamine, or dipropylamine.

3. A compound of the formula,



4. A method for preparing the compound according to Claim 1, which comprises reacting 1 mole of a cyanuric halide with 2 moles of 3-methoxy-4-aminoazobenzene-3'-sulfonic acid and 1 mole of an alkanolamine in either order.

5. A method for preparing the compound according to any one of Claims 1 to 3 substantially as described in Examples 1 to 3.

6. A process for dyeing cellulosic materials, characterized by using the compound according to any one of Claims 1 to 3.

7. A process according to Claim 6 substantially as described in Examples 4 to 6.

8. The process for dyeing cellulosic materials according to Claim 6 or 7 wherein said materials are paper and paper pulp.

9. Cellulosic materials dyed with the compound according to any one of Claims 1 to 3.

10. Cellulosic material dyed according to the process claimed in any one of claims 6 to 8.

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